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Title of Invention: Color ink for an ink jet printer and  
a picture-baked product using the ink

[Abstract]

A color ink for an ink jet printer free of clogging and capable of drawing patterns and pictures of high density and high quality is provided. The color ink contains at least six elements which are an inorganic pigment adapted to develop color upon baking, glass frit as a melting agent, water and a water-soluble medium as solvents, an alcohol for accelerating drying, a dispersant for suppressing the precipitation of the inorganic pigment and the glass frit, and a defoaming agent for suppressing the generation of bubbles, the mixture of the inorganic pigment and the glass frit being set in particle diameter in the range of 0.3 to 2  $\mu\text{m}$ .

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the color ink for ink jet printers which fitted pottery, glass, porcelain enamel, a ceramic product, building materials of a tile and others, etc. giving pictures and a pattern.

[0002]

[Description of the Prior Art] Conventionally, encaustic formation of a ceramic product has a common method of carrying out hand-drawn [ of the mixture of an inorganic pigment and a glass frit ] with pen etc., or using screen-stencil. The skilled engineer is needed even if it is a simple pattern, in order to form two or more ceramic products of the same pattern in the case of the approach by hand-drawn. Although screen printing has spread widely as a means to print [ two or more ], by this approach, platemaking is complicated and remarkable time amount and a remarkable effort are needed. Therefore, a sex is not only missing instance, but in the case of few lot many forms, there is a fault to which the unit price of one product becomes high. Moreover, by this approach, an encaustic forming face is restricted to a smooth side, and cannot form a pattern in a concave convex.

[0003] Then, it is suitable for encaustic formation of few lot many forms, and the ink for ink jet printers in which a concave convex can also form a pattern is proposed (the patent No. 2743330 official report). A metal pigment is mixed, and this ink is smaller than the nozzle diameter of an ink jet printer in a maximum grain size, and it mixes a dispersant at same rate as a metal pigment ten to 20% of the weight while it comes to mix at least 3 elements of the dispersant for preventing precipitate of this metal pigment with water or an oil, and the metal pigment of the property which will be colored and established if it calcinates and sets the mean diameter of a metal pigment as 6 micrometers.

[0004]

[Problem(s) to be Solved by the Invention] However, when it is going to draw to an object side with the ink jet printer of 120dpi, using the above-mentioned ink, there is a problem that nozzle opening starts blinding immediately and serves as use impossible. Although the nozzle diameter of the ink jet printer of 120dpi is about 60 micrometers and the metal pigment whose mean particle diameter is 6 micrometers is the magnitude which may be passed easily, in fact, the particle of a metal pigment condenses to nozzle opening, and produces blinding. Therefore, in the case of the above-mentioned ink, it could be used only with the ink jet printer of a low consistency with a big nozzle diameter, but it had the fault that a minute pattern or a minute picture could not be drawn.

[0005] Moreover, since the particle diameter of a metal pigment is large in the case of conventional ink, a metal pigment tends to precipitate. Therefore, a dispersant must be mixed at same rate as a metal pigment, and that there are many dispersants has also become the cause to which drawing quality is reduced.

[0006] Moreover, since the above-mentioned ink does not contain a glass component, ink is sprayed on the object side in which the glass layer was formed beforehand, and welding will be carried out to a glass layer at the same time it makes the metal pigment of ink calcinate and color. However, now, it can be used only for the object side which has a glass layer beforehand.

[0007] Then, the purpose of this invention does not have blinding, is high-density and is to offer the color ink for ink jet printers which can draw the pattern and picture of high quality. Moreover, other purposes are to offer the color ink for ink jet printers which can draw also to the object side which does not have a glass layer.

[0008]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, invention according to claim 1 contains at least the inorganic pigment and solvent which color by baking, and the dispersant which controls precipitate of an inorganic pigment, and offers the color ink for ink jet printers characterized by being in within the limits whose particle diameter of an inorganic pigment is 0.3-2 micrometers. Moreover, invention according to claim 4 contains at least the dispersant which controls precipitate of the inorganic pigment colored by baking, the glass frit as a welding agent, a solvent, an inorganic pigment, and a glass frit, and offers the color ink for ink jet printers characterized by

being in within the limits whose particle diameter of the mixture of an inorganic pigment and a glass frit is 0.3-2 micrometers.

[0009] When particle diameter mixed the inorganic pigment within the limits which are 0.3-2 micrometers, the solvent, and the dispersant, it became liquefied ink suitable for an ink jet printer, and even if it made the amount of a dispersant fewer than an inorganic pigment, precipitate of an inorganic pigment was prevented. Moreover, when this ink was used for the ink jet printer of 120dpi, clear drawing could be obtained and blinding was also canceled.

[0010] By the way, if particle size of the inorganic pigment which is a formed element is made small, the ink jet printer of high density will also become usable from 120dpi, but if particle size of an inorganic pigment is made not much small too much, coloring will worsen and the visibility of drawing will fall. When this invention person experimented and the particle diameter of an inorganic pigment was set to less than 0.3 micrometers, the color enhancement of inorganic pigment original was not obtained, but it became unsuitable at drawing. So, the particle diameter of an inorganic pigment was set to 0.3 micrometers or more in this invention.

[0011] Since mean particle diameter was very small like claim 2 when the mean particle diameter of an inorganic pigment was set as about 0.5 micrometers, the dispersibility of an inorganic pigment became much more good, and the homogeneity of coloring by each injected dot improved. Like claim 3, it is desirable for an inorganic pigment to carry out 10-60 weight section content to the solvent 100 weight section. It is because it will become easy to precipitate if coloring becomes inadequate [ under 10 weight sections ] and 60 weight sections are exceeded. Therefore, very clear drawing can be obtained by considering as the above-mentioned range.

[0012] Even when the glass frit as a welding agent other than an inorganic pigment, a solvent, and a dispersant is included and it does not have a glass layer in an object side like claim 4, welding of the ink can be carried out and it can be made to color certainly. It can be used that there is no blinding also in the ink jet printer of high density than 120dpi by carrying out the particle diameter of the mixture of an inorganic pigment and a glass frit within the limits of 0.3-2 micrometers also in this case.

[0013] Like claim 7, when a solvent contains water-soluble MEJUMU other than water, there is an advantage which can adjust ink to the viscosity suitable for an ink jet printer. In addition, since water-soluble MEJUMU is burned down by baking, the quality of drawing is not affected. the ink on which it had and sprayed quick-drying when the alcohol for making ink promote desiccation was contained like claim 8 -- liquid -- there is an advantage that it can prevent that wake up whom etc. and drawing is confused.

[0014] Generally, a bubble will be produced if the surface tension of a liquid becomes small. Since it melted into water, and surface tension was made small and two or more kinds of things are mixed when a solvent contains water-soluble MEJUMU (for example, glycols), foaming is produced. When a bubble arises in ink, it becomes impossible to inject with an ink jet printer. So, at claim 9, by adding the defoaming agent which controls generating of air bubbles in ink, the air bubbles generated from water-soluble MEJUMU can be removed beforehand, and it can inject good with an ink jet printer.

[0015] Like claim 10, it draws to an object with an ink jet printer using the color ink for ink jet printers according to claim 1 to 9, and if it calcinates above the temperature to which the above-mentioned inorganic pigment colors this object, a drawing baking object can be acquired. This drawing is very excellent in weatherability, and while being able to draw a high-definition clear pattern and a clear high-definition picture on this baking object, even if it uses it in the open air, on it, it can maintain the drawing quality stabilized for a long period of time. In addition, what is necessary is just to have the thermal resistance more than the coloring temperature of an inorganic pigment and the melting temperature of a glass frit, such as pottery, glass, porcelain enamel, a tile, and a fine-ceramics product, as an object.

[0016]

[Embodiment of the Invention] Below, an example of the color ink for ink jet printers concerning this invention is shown. The ink of this example contains the defoaming agent for removing beforehand the dispersant which controls precipitate of the solvent which consists of alcohol for carrying out desiccation to the inorganic pigment, the glass frit as a welding agent, the water, and water-soluble MEJUMU which color by baking and can be burned early, an inorganic pigment, and a glass frit, and the air bubbles generated from MEJUMU.

[0017] As the particle diameter of the inorganic pigment which is a formed element, and a glass frit is shown in drawing 1 and drawing 2, it is prepared in the range of 0.3-2 micrometers, and the mean particle diameter is set as about 0.5 micrometers. To the solvent 100 weight section, 10 - 60 weight section and a dispersant are mixed in the 0.1 - 0.5 weight section, and the defoaming agent is mixed for the mixture of an inorganic pigment and a glass frit at a rate of the 0.1 - 0.5 weight section.

[0018] Drawing 1 shows particle size distribution and the weight ratio of each concrete particle diameter is calculated as follows with reference to drawing 2. For example, the 1.676 micrometers - 1.371 micrometers weight ratio which is a maximum grain size is  $100-99.904=0.096$  (%).

Come out, it is and a 1.676 micrometers - 0.501 micrometers weight ratio is  $100-50.948=49.052$  (%).

It becomes. In addition, the minimum particle diameter of the inorganic pigment used this time and a glass frit was 0.274 micrometers.

[0019] As an inorganic pigment, as a metallic oxide, crystal structures, such as oxidization copper and cobalt oxide, are mentioned as sulfides, such as a spinel, SUFEIN, pyrochlore, RUCHIRU, a ply deweylite, phosphate, a phenakite, a PERIKU ball race, olivine, baddeleyite, borate, corundum, and zircon, and selenium red etc. is mentioned as cadmium-selenide compounds, such as cadmium yellow. Moreover, a fluorescent substance pigment, a \*\*\*\*\* pigment, etc. may be used.

[0020] As a glass component, the following compounds are mentioned as what raises the welding nature of the above-mentioned inorganic pigment. As an alkali metal compound, oxidization silicon, a boric acid, a zirconium dioxide, titanium oxide, etc. are mentioned as acidic components, such as an aluminum oxide and an aluminum hydroxide, as neutral components, such as a barium carbonate, a strontium carbonate, a calcium carbonate, a magnesium carbonate, and a zinc oxide, as alkaline earth metals, such as a lithium carbonate, a sodium carbonate, potassium carbonate, a lead oxide, and bisumuth oxide. Moreover, borax, a feldspar, a kaolin, etc. are mentioned as a double compound component. These independent or things mixed [ two or more ] are dissolved, and the so-called frit is produced and used.

[0021] independent [ in a glycol system, a glycerol system, a poly vinyl alcohol system, etc. ] as water-soluble MEJUMU -- or it can be mixed and used. In addition, MEJUMU used for this invention is not limited to these, and the MEJUMU component currently conventionally used for well-known ink can be used for it.

[0022] Drawing 3 shows the relation of the viscosity of ink and the content of an inorganic pigment which made content of water-soluble MEJUMU the parameter. In addition, the content of water-soluble MEJUMU is weight % to a solvent. When the content of MEJUMU is 10% and the content of MEJUMU becomes 20% to the viscosity of ink being mostly stable in 20 - 30cp regardless of the content of a pigment so that clearly from drawing, it turns out that the viscosity of ink becomes high suddenly at 50% or more, and the content of a pigment exceeds 50cp. Since the viscosity of the ink for ink jet printers has desirable 20 - 50cp extent, as for the content of water-soluble MEJUMU, considering as 10 - 30% is desirable.

[0023] As a dispersant, an inorganic system dispersant like metaphosphoric-acid 6 sodium and sodium diphosphate and an organic system dispersant like diethylamine are usable. For example, foaming of ink can be prevented by adding optimum dose beforehand, using a polyglycol system as a defoaming agent.

[0024] When 10 - 60 weight section and a dispersant were mixed in the 0.1 - 0.5 weight section and the defoaming agent was mixed for the mixture of an inorganic pigment and a glass frit at a rate of the 0.1 - 0.5 weight section to the solvent (water, water-soluble MEJUMU, alcohol) 100 weight section as mentioned above, it was checked that the shape of usable liquid is presented with an ink jet printer, and the mixture of an inorganic pigment and a glass frit is almost in a distributed condition. By in addition to it, making the particle diameter of an inorganic pigment and a glass frit into the range of 0.3-2 micrometers, and setting the mean particle diameter to about 0.5 micrometers, blinding was not carried out to the nozzle of an ink jet printer, but good injection was able to be performed continuously. Moreover, by adding alcohol to a solvent, quick-drying [ of ink ] was urged and degradation of drawing quality has been prevented.

[0025] After using the ink jet printer of for example, 120dpi for ceramic products, such as pottery, and drawing using the above-mentioned ink, when the ceramic product was calcinated at 750-1250 degrees C, drawing of a clear and minute color picture was able to be obtained. Moreover, in an ink jet printer, blinding did not occur at all.

[0026] In addition, various burning temperature is selected with ink and an object. For example, since it fuses at low temperature (for example, about 600 degrees C) comparatively when an object is glassware, it is necessary to use the inorganic pigment and frit which are colored below at the temperature which an object fuses. Moreover, it is desirable to calcinate at an elevated temperature (for example, near about 1200 degree C) in the ink for under glaze decoration which paints the field where the cover coat has not taken a front face, and to calcinate at low temperature (near about 800 degree C) comparatively in the ink for on-glaze decoration which paints the field where the cover coat took the front face.

[0027]

[Example] Next, the example of manufacture of the ink concerning this invention is shown. In addition, the ink of this invention is not limited to these.

(Example 1 of manufacture of ink)

A solvent (water, glycols mixture) 100 weight sections alcohol Ten weight sections pigment (spinel pigment) and the mixture of a frit (lead oxide, alkali metal, alkaline earth metal, an alumina, a boric acid, silica) 21 weight partial powder (sodium diphosphate) 0.2 weight sections defoaming agent (anti froth F233 Dai-Ichi Kogyo Seiyaku Co., Ltd. make) The screen of 250 meshes was passed for the 0.5 weight sections above-mentioned pigment and the frit after mixing by the mixer. Then, this powder was fed into the solvent with the dispersant and the defoaming agent, it stirred and cyanogen pigment ink was created.

[0028]

(Example 2 of manufacture of ink)

A solvent (water, glycols mixture) 100 weight sections alcohol Ten weight sections pigment (SUFEN pigment) and the mixture of a frit (lead oxide, alkali metal, alkaline earth metal, an alumina, a boric acid, silica) 50 weight partial powder (sodium diphosphate) 0.2 weight sections defoaming agent (anti froth F233 Dai-Ichi Kogyo Seiyaku Co., Ltd. make) Magenta pigment ink was created by the same approach as cyanogen pigment ink using the 0.5 weight sections above-mentioned ingredient.

[0029]

(Example 3 of manufacture of ink)

A solvent (water, glycols mixture) 100 weight sections alcohol Ten weight sections pigment (zircon pigment) and the mixture of a frit (lead oxide, alkali metal, an alumina, a boric acid, silica) 50 weight partial powder (sodium diphosphate) 0.2 weight sections defoaming agent (anti froth F233 Dai-Ichi Kogyo Seiyaku Co., Ltd. make) Yellow pigment ink was created by the same approach as cyanogen pigment ink using the 0.2 weight sections above-mentioned ingredient.

[0030] The ink of the above cyanogen (C), a Magenta (M), and yellow (Y) in three primary colors was able to be created according to the individual, and the clear RGB color picture was able to be drawn by spraying these ink on the same dot with an ink jet printer alternatively. That is, the mixed color of Y+M=R (red), Y+C=G (Green), and M+C=B (blue) was able to be obtained easily. When in the case of conventional inorganic color ink it injected from nozzles, such as an ink jet printer, and drew and calcinated on a screen, it was difficult to be hard to color two colors on the same dot on a drawing surface as neutral colors, and to obtain mixed colors R, G, and B on a screen. Therefore, in the former, since it was necessary to use the ink other than Y, M, and C, such as R, G, and B, and to accumulate the ink of these large number in an ink jet printer, it was [ that structure is complicated and ] large-sized. If the ink of this invention is used, since neutral colors can be made to color easily in the ink of C, M, and Y in three primary colors, small and simplification of an ink jet printer can be done, and the number of nozzles can be lessened. In addition, it is also possible to use an oil although water was used as a solvent in the above-mentioned example.

[0031]

[Effect of the Invention] It does not make the nozzle of an ink jet printer generate blinding so that clearly [ in the above explanation ] while it can prevent precipitate of an inorganic pigment, since the color ink for ink jet printers according to claim 1 contained at least solvents, such as an inorganic pigment, water, etc. which color by baking, and the dispersant which controls precipitate of an inorganic pigment and made the particle diameter of an inorganic pigment within the limits of 0.3-2 micrometers, but direct writing can be carried out also in respect of an irregular object. Since especially the ink of this invention can be used also for the ink jet printer of the high density exceeding 120dpi which was not able to be used in the former, it is high-density and the pattern and picture of high quality can be drawn.

[0032] Moreover, since the color ink for ink jet printers according to claim 4 made the particle diameter of the mixture of an inorganic pigment and a glass frit other than an inorganic pigment, a solvent, and a dispersant within the limits of 0.3-2 micrometers including the glass frit as a welding agent, it has the description that it can draw also to the object side which does not have a glass layer in addition to the effectiveness of claim 1.

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[Translation done.]